

## PATENT ABSTRACTS OF JAPAN

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### (54) THERMALLY SHRINKABLE POLYESTER-BASED FILM

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a thermally shrinkable polyester-based film which can exhibit a good shrunk finish property, even when used for full labels, has a function capable of reinforcing a shrunk-covered container, and has a function capable of ensuring the visibility of contents and simultaneously preventing the deterioration of the qualities of the container contents due to UV rays, and to provide a thermally shrinkable label using the film.

SOLUTION: This thermally shrinkable polyester-based film is characterized by having (A) a thermal shrinkage rate of 10 to 50 % in the maximum shrinkage direction in 70° C hot water, (B) a thermal shrinkage rate of  $\geq 75$  % in the maximum shrinkage direction and a shrinkage rate of  $\leq 10$  % in the direction orthogonal to the maximum shrinkage direction in 85° C hot water, (C) a thermal shrinkage rate difference  $\Delta$  (%)

of 10 to 20 %, wherein  $\Delta$  is represented by expression:  $\Delta = X_0 - X_{10}$ ;  $X_0$  (%) is a thermal shrinkage rate in the maximum shrinkage direction in 95° C hot water;  $X_{10}$  (%) is a thermal shrinkage rate of the 10 % thermally shrunk film in 95° C hot water, (D) light transmittance of  $\leq 20$  % and  $\leq 60$  % at wavelength of 380 nm and 400 nm, respectively, and (E) haze of  $\leq 15$  %.

## CLAIMS

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[Claim(s)]

[Claim 1]

A heat contraction nature polyester system film being a heat contraction nature polyester system film, and being what satisfies following (A) - (E).

(A) A heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up about a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is 10 to 50%.

(B) About a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square. A heat shrinkage rate of a direction to which a maximum shrinkage direction and a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up cross at right angles not less than 75% is 10% or less.

(C) A sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, And about a sample which cut off a film made [ a maximum shrinkage direction ] to carry out heat contraction 10% 10 cm x 10 cm in the shape of a square. The heat shrinkage rate difference  $\Delta$  (%) shown by a lower formula when making into  $X_0$  (%) and  $X_{10}$  (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up, respectively is 10 to 20%.

$$\Delta = X_0 - X_{10}$$

(D) Light transmission whose light transmission with a wavelength of 380 nm is 20% or less and the wavelength of 400 nm is 60% or less.

(E) Haze is 15% or less.

[Claim 2]

When a thermal-shrinkage-stress value about this direction of a film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind, The heat contraction nature polyester system film according to claim 1 whose maximum-heat-shrinkage-stress value is 7 or more MPa.

[Claim 3]

The heat contraction nature polyester system film according to claim 1 or 2 whose thickness distribution which specifies thickness displacement measurement in a maximum shrinkage direction of a film below when a specimen 50 cm in length and 5 cm in width is followed is 6% or less.

Thickness distribution = [(the maximum thickness-minimum thickness) /average thickness] x100

[Claim 4]

The heat contraction nature polyester system film according to any one of claims 1 to 3 whose melt resistivity value in 275 \*\* is below  $0.70 \times 10^8$  omega-cm.

[Claim 5]

A heat contraction nature label using the heat contraction nature polyester system film according to any one of claims 1 to 4.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the heat contraction nature label using the suitable heat contraction nature polyester system film for a label use, and this film.

[Background of the Invention]

[0002]

The heat contraction nature plastic film is widely used for the use of a shrink package, a shrink label, etc. using the character contracted with heating. Oriented films especially, such as a polyvinyl chloride system film, a polystyrene system film, and a polyester system film, In various containers, such as a polyethylene terephthalate (PET) container, a polyethylene container, and glassware, it is used for the purpose of a label, a cap seal, or an accumulation package (for example, patent documents 1).

[0003]

However, the polyvinyl chloride system film has problems, like heat resistance is low,

generates hydrogen chloride gas at the time of incineration, or causes dioxin. If a heat contraction nature VCM/PVC system resin film is used as shrink labels, such as a PET container, when carrying out recycling use of the container, there is a problem that a label and a container must be separated.

[0004]

On the other hand, although the point whose result appearance nature after contraction of a polystyrene system film is good can be evaluated, since it is inferior to solvent resistance, the ink of a special presentation must be used in the case of printing. It is necessary to incinerate polystyrene system resin at an elevated temperature and also and it has the problem that a lot of black smokes and nasty smells at the time of incineration occur.

[0005]

The polyester system film without these problems is dramatically expected as a shrink label which replaces a polyvinyl chloride system film and a polystyrene system film. The amount used is also increasing with the amount-used increase of a PET container.

[0006]

With the gestalt of this film roll, after manufacture, these heat contraction nature films are once rolled round by rolled form, are sent to the presswork of various patterns, and after the end of printing, If needed, slit processing is carried out according to the size of the label etc. which are used for a final product, and the right-and-left-ends part of a film is further piled up by solvent bonding or other means, a seal is carried out, it is made a tube shape object, the thing of this tube shape object is judged, and it is processed into the gestalt of a label, a bag, etc. And the contraction tunnel (steam tunnel) of the type which equips a container with a label or a saccate thing and to which heat contraction of the steam is sprayed and carried out, A hot wind is sprayed, the inside of the contraction tunnel (hot wind tunnel) of the type which carries out heat contraction is put on a band conveyor etc., and is passed, heat contraction is carried out, and it is made to stick to a container.

[0007]

By the way, from a viewpoint of recycling, use of a colored PET bottle follows on being restricted, it replaces with coloring of the bottle itself, and the demand (what is called a full label use) of a wrap is also growing with the label made from a heat contraction nature polyester system film in the great portion of bottle side. However, the side shape of a PET bottle is various, and since an outer diameter changes in arbitrary height positions, the grades of contraction that at least one label which covers the

bottle whose number is one is required differ in the height position of a bottle. For this reason, even when it has conventionally better shrink characteristics than elegance and is used for covering of the bottle of complicated side shape, the heat contraction nature polyester system film which can demonstrate the outstanding contraction result nature is called for.

[0008]

For example, with the PET bottle of the bevel use, the case where label wearing and contraction are performed all over a drink charging line is increasing for the productivity drive. Since such a charging line is a high speed, wearing and contraction of a label also become high-speed, and is in the tendency for contraction to be performed for a short time. Therefore, the heat contraction nature polyester system film is asked also for the physical properties which can be equal to high-speed wearing, and the contraction performance which serves as high contraction for a short time.

[0009]

In addition, these days, the operation which reinforces these containers is also being expected from the label used for various containers, such as a PET bottle. However, the label obtained from the conventional heat contraction nature polyester system film cannot satisfy such a reinforcing operation.

[0010]

These days, using the above-mentioned label is also performed in order to prevent the contents (drink etc.) with which the container was filled up deteriorating by the ultraviolet rays which enter from the container outside, or coloring. Although the shrink film made from polyvinyl chloride ultraviolet-rays cut type was common conventionally, the demand to what is constituted from raw materials other than polyvinyl chloride by the Reason mentioned above is increasing. Although the ultraviolet-rays cut nature demanded concretely is changed according to contents, since deterioration, coloring, etc. take place easily for example, by the ultraviolet rays of the long wavelength of 360-400 nm in contents in the case of foodstuffs or a drink, its characteristic which can omit the ultraviolet rays of such a wavelength band is desirable. However, there was nothing that can omit the ultraviolet rays of such a long wavelength region in the conventional label made from polyester.

[Patent documents 1] JP,H7-138388,A (paragraph numbers 0001-0005)

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0011]

This invention is made in light of the above-mentioned circumstances, and the

purpose, Even if it uses for a full label, can demonstrate good contraction result nature, and it has a function in which the container which carried out contraction covering can be reinforced, It is in providing the heat contraction nature label using the heat contraction nature polyester system film which has a function in which the quality degradation by the ultraviolet rays of container contents can be prevented, and this film, securing the visibility of contents furthermore.

[Means for Solving the Problem]

[0012]

A heat contraction nature polyester system film of this invention which could attain the above-mentioned purpose has a gist at a place which is what satisfies following (A) - (E).

(A) A heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 °C warm water, and it pulled up about a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, and it is immersed for 10 seconds subsequently to underwater [ 25 °C ] and pulls up is 10 to 50%.

(B) About a sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square. A heat shrinkage rate of a direction to which a maximum shrinkage direction and a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 °C warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 °C ] and pulls up cross at right angles not less than 75° is 10° or less.

(C) A sample of a heat contraction nature polyester system film cut off 10 cm x 10 cm in the shape of a square, And about a sample which cut off a film made [ a maximum shrinkage direction ] to carry out heat contraction 10% 10 cm x 10 cm in the shape of a square. The heat shrinkage rate difference  $\Delta$  (%) shown by a lower formula (1) when making into  $X_0$  (%) and  $X_{10}$  (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 °C warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 °C ] and pulls up, respectively is 10 to 20%.

$$\Delta = X_0 - X_{10} \quad (1).$$

(D) Light transmission whose light transmission with a wavelength of 380 nm is 20% or less and the wavelength of 400 nm is 60% or less.

(E) Haze is 15% or less.

[0013]

The above-mentioned heat contraction nature polyester system film, When a

thermal-shrinkage-stress value about this direction of this film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in temperature of 90 \*\*, and blow-off speed ]/second hot wind, it is preferred that a maximum-heat-shrinkage-stress value is 7 or more MPa.

[0014]

It is recommended that thickness distribution as which the above-mentioned heat contraction nature polyester system film specifies thickness displacement measurement in a maximum shrinkage direction of this film at a lower ceremony (2) when a specimen 50 cm in length and 5 cm in width is followed is 6% or less. Thickness distribution = [(the maximum thickness-minimum thickness) /average thickness] x100 (2).

[0015]

In addition, as for the above-mentioned heat contraction nature polyester system film, it is preferred that a melt resistivity value in 275 \*\* is below  $0.70 \times 10^8$  omega-cm.

[0016]

A heat contraction nature label using the above-mentioned heat contraction nature polyester system film is also included by this invention.

[Effect of the Invention]

[0017]

Even if the heat contraction nature polyester system film of this invention is a case where high contraction is required selectively, it can acquire beautiful contraction result appearance by contraction in a low temperature region comparatively. Film production nature and processability are good. The heat contraction nature label obtained from the heat contraction nature polyester system film of this invention is excellent in the reinforcing effect of a covering container, and the effect which controls the quality degradation of the container contents by ultraviolet rays. The visibility of the contents of a covering container is also good.

[0018]

Therefore, the heat contraction nature polyester system film and heat contraction nature label of this invention are suitable for various covering labels including full labels, such as a PET bottle, etc.

[Best Mode of Carrying Out the Invention]

[0019]

The heat contraction nature polyester system film of this invention is obtained using the mixture of the single copolymerized polyester which uses as a main component

unit the ester unit formed from a publicly known polyvalent carboxylic acid component and a polyhydric alcohol component, or two or more polyester.

[0020]

The heat contraction nature polyester system film of this invention is 10% or less towards the maximum shrinkage direction and heat shrinkage rate measured on condition of the above (A) and (B) crossing at right angles not less than 75% in less than more than (A):10%50% and (B):maximum shrinkage direction. With such a film, the heat contraction nature label which serves as high contraction by short-time processing comparatively can be provided.

[0021]

Usually, at the process which carries out covering contraction to a container etc., the label made from a heat contraction nature film. In an above-mentioned hot wind tunnel, the inside of the hot wind of about 120-200 °C and about 2-20 m/second of wind speeds is passed in about 2 to 20 seconds, and it carries out by passing the inside of about 75-95 °C and the steam of about 0.5-20 MPa of pressures in about 2 to 20 seconds in a steam tunnel. (A) And the film with which all the heat shrinkage rates of (B) are satisfied of a mentioned range, For example, containers, such as a PET bottle which has complicated side shape, are received, Use this the greater part of side as a heat contraction nature label of a wrap sake, or, Even if it uses it as a heat contraction nature label for containers which has the side shape which requires partial very high contraction of a wrap label for the side (even if it uses it for for example, the full label for PET bottles, the full label for glass bottles, etc.), Very beautiful contraction result appearance can be attained under such contraction conditions usually performed.

[0022]

That is, when the heat shrinkage rate measured on condition of (A) is less than a mentioned range, low-temperature shrinkage characteristics will need to become insufficient, and it will be necessary to make high temperature at the time of label covering contraction, and is not desirable. On the other hand, when the heat shrinkage rate measured on condition of (A) exceeds a mentioned range, it is in the tendency which defects, such as a jump (shift up when a film contracts rapidly) of the label by heat contraction, produce. As for the heat shrinkage rate measured on condition of (A), it is preferred that it is [ not less than 15% ] 40% or less.

[0023]

When the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B) is less than a mentioned range, when a PET bottle etc. are made to carry out covering contraction as a label, it is in the tendency which the shortage of



contraction produces in the portions (for example, opening part of a bottle, etc.) as which bigger contraction is required, for example. It is not less than 78% preferably. As for the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B), it is preferred that it is 95% or less.

[0024]

When the heat shrinkage rate (direction-crossing-at-a-right-angle heat shrinkage rate) of the direction which intersects perpendicularly with the maximum shrinkage direction measured on condition of (B) exceeds a mentioned range, the appearance defect by TATEHIKE occurs. "TATEHIKE" is that the length of the label after contraction becomes irregular, and the appearance defect which draws the line where the upper bed edge of the label after making a PET bottle etc. carry out covering contraction curves downward, or draws the line where a lower end edge curves upward is said. As for the direction-crossing-at-a-right-angle heat shrinkage rate measured on condition of (B), it is preferred that it is 7% or less.

[0025]

In addition, the heat contraction nature polyester system film of this invention, The heat shrinkage rate of the measured maximum shrinkage direction on the above conditions (C) about the film before heat contraction  $X_0$  (%), When the heat shrinkage rate of the maximum shrinkage direction measured on the above conditions (C) is made into  $X_{10}$  (%) about the film to which the maximum shrinkage direction was made to once carry out heat contraction of the film before heat contraction 10%, the heat shrinkage rate difference delta (%) expressed with an upper type (1) is not less than 10% of 20% or less. If the above-mentioned heat shrinkage rate difference delta is a heat contraction nature polyester system film which becomes in a mentioned range, the heat contraction nature label which has a reinforcing effect of a covering container can be obtained.

[0026]

In the heat contraction nature label obtained from the heat contraction nature polyester system film which is less than a mentioned range, the above-mentioned heat shrinkage rate difference delta becomes insufficient [ the reinforcing effect of the container after covering contraction ]. In the heat contraction nature polyester system film of this invention, the desirable heat shrinkage rate difference delta is 17% or less. Since the above-mentioned heat shrinkage rate  $X_{10}$  is a value measured using the film which carried out heat contraction 10%, the minimum of the heat shrinkage rate difference delta is not less than 10%.

[0027]

Incidentally with the usual heat contraction nature polyester system film. Once carrying out heat contraction 10%, the final heat shrinkage rate (sum total of 10% of the first heat shrinkage rate, and the 2nd heat shrinkage rate) at the time of carrying out heat contraction again, It falls more greatly than the heat shrinkage rate in the case of having shrunk the film before heat contraction thoroughly on the same heat contraction conditions (that is, the above-mentioned heat shrinkage rate difference delta will exceed a mentioned range). In the film of this invention, the presentation of the polyester used for a film is made suitable so that it may mention later, and it is supposed that the extension conditions of a film are controlled and the heat shrinkage rate difference delta in a mentioned range will be secured.

[0028]

The above-mentioned "heat shrinkage rate of a maximum shrinkage direction" means the heat shrinkage rate in the direction which the sample contracted most, and a maximum shrinkage direction and direction crossing at a right angle are decided by the length of a square lengthwise direction or a transverse direction. A heat shrinkage rate (%) a sample (10 cm x 10 cm) by the heat shrinkage rate measured on condition of (A) in 70 °C ± 0.5 °C warm water, In the heat shrinkage rate measured on condition of (B), in 85 °C ± 0.5 °C warm water, The length of a film immediately after being immersed for 5 seconds and carrying out heat contraction according to no load condition into 95 °C ± 0.5 °C warm water, respectively in heat shrinkage rate  $X_0$  measured on condition of (C), after being immersed in 25 °C underwater [ ± 0.5 °C ] for 10 seconds by no load condition, and the lateral length are measured, and it is a lower type.

Heat shrinkage rate =  $100 \times (\text{length after the length-contraction before contraction}) / (\text{length before contraction})$

It is the value which was boiled, and was followed and calculated.

[0029]

The above-mentioned heat shrinkage rate  $X_{10}$  used for calculation of the heat shrinkage rate difference delta is measured as follows.

[0030]

First, the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is produced. The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum shrinkage direction. The film after decision is fixed with a described [ above ] type. Immobilization is performed by slacking a film so that the both ends

which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 °C warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 °C underwater [ 0.5 °C ], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained.

[0031]

A sample (10 cm x 10 cm) is judged from the obtained film, heat shrinkage rate  $X_{10}$  is measured using this sample by the same method as the above-mentioned heat shrinkage rate  $X_0$ , and the heat shrinkage rate difference  $\Delta$  is computed by an upper type (1).

[0032]

As for each of time until it goes into a sample cutting process from the making process of the film made [ the maximum shrinkage direction ] to carry out heat contraction 10%, and time until it goes into the heat contraction process in the conditions of (C) from a sample cutting process, it is desirable to consider it as a short time as much as possible. When keeping the sample judged when the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% was kept to a sample cutting process to a heat contraction process, it is in an atony state, and it places in the air and under the environment of 25 °C or less, and unnecessary heat contraction is kept from arising.

[0033]

The heat contraction nature polyester system film of this invention is 20% or less (0% is included) in light transmission with a wavelength of 380 nm, and is 60% or less (0% is included) in light transmission with a wavelength of 400 nm. Deterioration, coloring, etc. of the contents (foodstuffs, a drink, etc.) of a container may mainly be produced by the ultraviolet rays of a 360–400-nm wavelength band as mentioned above. So, in the film of this invention, it has good ultraviolet-rays cut nature because below the above-mentioned upper limit carries out light transmission with a wavelength of 380 nm and 400 nm, and offer of the heat contraction nature label which can control the quality degradation of container contents was enabled.

[0034]

That is, in the film in which light transmission with a wavelength of 380 nm and/or light transmission with a wavelength of 400 nm exceed the above-mentioned upper limit,

the heat contraction nature label which can fully control the quality degradation of the container contents by ultraviolet rays cannot be provided. As for light transmission with a wavelength of 380 nm, it is more preferred that it is 10% or less, and it is still more preferred that it is 5% or less. As for light transmission with a wavelength of 400 nm, it is more preferred that it is 50% or less, and it is still more preferred that it is 30% or less. When light transmission with a wavelength of 400 nm is too small, a film may color. Therefore, in order to prevent coloring of such a film, it is preferred to make light transmission with a wavelength of 400 nm into not less than 5%, it is more preferred to consider it as not less than 10%, and it is still more preferred to consider it as not less than 20%.

[0035]

Each of above-mentioned light transmission is values calculated by the measuring method later mentioned in working example.

[0036]

In addition, Hays of the heat contraction nature polyester system film of this invention is 5% or less still more preferably 10% or less preferably 15% or less. Since the film of this invention is excellent in ultraviolet-rays cut nature like the above, and Hays is below the above-mentioned upper limit, when it excels in the permeability over available light (visible light) etc. and uses for the label for container covering, its visibility of container contents is good. Above-mentioned Hays is a value calculated by the measuring method later mentioned in working example.

[0037]

Above-mentioned ultraviolet-rays cut nature and natural light transmittance state, A film is made to contain ultraviolet-rays cut agents (a low molecule system ultraviolet-rays cut agent, the Polymer Division system ultraviolet-rays cut agent, an inorganic system ultraviolet-rays cut agent, etc.), and a kind, a content gestalt, etc. of an ultraviolet-rays cut agent are securable by choosing appropriately (for details, it mentions later).

[0038]

In the heat contraction nature polyester system film of this invention. When the thermal-shrinkage-stress value about this direction of the film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in the temperature of 90 \*\*, and blow-off speed ]/second hot wind, it is preferred that a maximum-heat-shrinkage-stress value is 7 or more MPa. If the above-mentioned maximum-heat-shrinkage-stress value is a film of 7 or more MPa, the heat

contraction nature label in which the reinforcing effect of the covering container was more excellent can be obtained. That is, the above-mentioned maximum-heat-shrinkage-stress value is in the tendency for the effect of reinforcing a covering container to fall, in the heat contraction nature label obtained from the film which is less than a mentioned range. As for the above-mentioned maximum-heat-shrinkage-stress value, it is more preferred that they are 10 or more MPa, and it is still more preferred that they are 11 or more MPa.

[0039]

The above-mentioned maximum-heat-shrinkage-stress value is measured by the following methods.

[1] From a heat contraction nature polyester system film, the length of a maximum shrinkage direction cuts down the specimen which are 200 mm and 20 mm in width.

[2] Heat the inside of the heating furnace of the tension tester (for example, product made from an Oriental energy machine "tensilon") provided with the hot wind type heating furnace at 90 °C.

[3] Stop air blasting and set a specimen in a heating furnace. The distance between zippers shall be 100 mm (fixed), and the length between zippers of a specimen and the distance between zippers slack a specimen, and set it so that it may be set to 1:0.9.

[4] Shut the door of a heating furnace promptly and resume air blasting (5 m/s in the temperature of 90 °C, and blow-off speed 10 l/min hot wind). Heat contraction of the specimen is carried out 10%, and the thermal shrinkage stress after this heat contraction is detected and measured.

[5] The maximum is read in a chart and let this be a maximum-heat-shrinkage-stress value (MPa).

[0040]

As for the heat contraction nature polyester system film of this invention, it is preferred that thickness is more uniform, and it is recommended that the thickness distribution which specifies the thickness displacement measurement in the maximum shrinkage direction of a film at an upper ceremony (2) when a specimen 50 cm in length and 5 cm in width is followed is 6% or less.

[0041]

Ten specimens which the above-mentioned thickness distribution is 50 cm in length and 5 cm in width, and make the maximum shrinkage direction of a film the length direction are created. About each specimen, a contact process thickness meter (for example, "KG60/A" by ANRITSU CORP.) is used. After measuring the thickness of the length direction continuously, outputting to a chart, asking for maximum thickness,

the minimum thickness, and average thickness from this output and computing thickness distribution using an upper type (2) from these, it is obtained by calculating the average value of the thickness distribution of ten specimens.

[0042]

In the film in which the above-mentioned thickness distribution exceeds 6%, it is presswork, the printability at the time of printing a multicolor pattern especially is inferior, and when piling up two or more colors, it is easy to carry out raw [ of the gap ]. In order to manufacture a label from the film of this invention, when carrying out solvent bonding and tube-ization-processing it, superposition of the adhesion part of a film becomes difficult. When the above-mentioned thickness distribution rolls round to rolled form according to a film manufacturing process in the film exceeding 6%, the difference of partial volume hardness arises and the slack and wrinkles of a film resulting from this occur, and also when it becomes impossible to use it as a heat contraction nature film, it is, 5% or less of the above-mentioned thickness distribution is still more desirable, and is desirable. [ especially 4% or less of ]

[0043]

It is preferred that the melt resistivity value in 275 \*\* is below  $0.70 \times 10^8$  omega-cm in the heat contraction nature polyester system film of this invention. Thus, if a melt resistivity value is small, it faces cooling the film which carried out melting extrusion from the extrusion machine with a casting roll, and the electrostatic adhesion of the film to a roll can be improved. Therefore, the stability of cooling solidification can be improved and casting speed (production rate) can be raised. As for a melt resistivity value, it is more preferred that it is below  $0.65 \times 10^8$  omega-cm, and it is still more preferred that it is below  $0.60 \times 10^8$  omega-cm.

[0044]

Film quality can also be raised, if a melt resistivity value is low and electrostatic adhesion is high. Namely, when electrostatic adhesion is low, the cooling solidification of a film becomes imperfect, exhaust air enters locally between a casting roll and a film, and there is a possibility that a pinner bubble (stripe-like defect) may occur in a film surface, but. If excelled in electrostatic adhesion, generating of said pinner bubble can be reduced and film appearance can be made good.

[0045]

In addition, the thickness of a film can be equalized, when a melt resistivity value is low enough and electrostatic adhesion is high enough. Namely, if the electrostatic adhesion to a casting roll is low, the thickness of the cast unstretched film original fabric will become uneven, and the heterogeneity of thickness will be expanded more

in the oriented film which extended this unstretched film, but. When electrostatic adhesion is high enough, thickness can be equalized also in an oriented film.

[0046]

In order to control the melt resistivity value of a film to a mentioned range, it is desirable to make an alkaline earth metal compound and the Lynn content compound contain in a film. Although at least an alkaline earth metal compound can lower a melt resistivity value, if the Lynn content compound is made to live together, a melt resistivity value can be lowered remarkably. Although the Reason for the ability to reduce a melt resistivity value remarkably by combining an alkaline earth metal compound and the Lynn content compound is not clear, by making the Lynn content compound contain, the quantity of a foreign matter can be decreased and it is presumed because the quantity of a charge carrier can be increased.

[0047]

As for the content of the alkaline earth metal compound in a film, it is preferred to use more than 40 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline-earth-metals atom  $M^2$ , for example, it is more preferred to be referred to as not less than 50 ppm, and it is still more preferred to be referred to as not less than 60 ppm. When there is too little quantity of an alkaline earth metal compound, it is to lower a melt resistivity value in the tendency which becomes difficult. Even if it increases content of an alkaline earth metal compound too much, the reduction effect of a melt resistivity value is saturated and it is in the tendency for evils, such as foreign matter generation and coloring, to become large rather. Therefore, as for the content of an alkaline earth metal compound, it is preferred to be referred to as 400 ppm or less on the basis of alkaline-earth-metals atom  $M^2$ , for example, it is more preferred to be referred to as 350 ppm or less, and it is still more preferred to be referred to as 300 ppm or less.

[0048]

As for the content of the Lynn content compound in a film, it is preferred to use more than 10 ppm (it is [ a mass basis and the following ] the same) on the basis of phosphorus atom P, for example, it is more preferred to be referred to as not less than 15 ppm, and it is still more preferred to be referred to as not less than 20 ppm. If there is too little quantity of the Lynn content compound, it may become difficult to fully lower a melt resistivity value, and the generated amount of a foreign matter cannot be reduced. Even if it increases content of the Lynn content compound too much, the reduction effect of a melt resistivity value will be saturated. Furthermore generation of a diethylene glycol is promoted, and since it is difficult to control the generated

amount moreover, there is a possibility of differing from what film properties were planning. Therefore, as for the content of the Lynn content compound, it is preferred to be referred to as 500 ppm or less on the basis of phosphorus atom P, for example, it is more preferred to be referred to as 450 ppm or less, and it is still more preferred to be referred to as 400 ppm or less.

[0049]

As for the mass ratio ( $M^2/P$ ) of alkaline-earth-metals atom  $M^2$  in a film, and phosphorus atom P, when lowering the melt resistivity value of a film with an alkaline earth metal compound and the Lynn content compound, it is desirable that it is 1.5 (1.7 or more [ 1.6 or more / Preferably / still more preferably ]) or more. By making a mass ratio ( $M^2/P$ ) or more into 1.5, a melt resistivity value can be reduced remarkably. If a mass ratio ( $M^2/P$ ) exceeds 5.0, the generated amount of a foreign matter may increase, or the generated amount of a foreign matter may increase, or a film may color. Therefore, as for a mass ratio ( $M^2/P$ ), it is preferred to use 5.0 or less, it is more preferred to use 4.5 or less, and it is still more preferred to use 4.0 or less.

[0050]

In order to lower the melt resistivity value of a film further, it is desirable to make an alkali metal compound contain in a film in addition to the above-mentioned alkaline earth metal compound and the Lynn content compound. Even if it makes a film contain an alkali metal compound independently, it cannot lower a melt resistivity value, but it can lower a melt resistivity value remarkably by adding to the coexistence system of an alkaline earth metal compound and the Lynn content compound. Although it is not clear about the Reason, it is presumed by forming a complex by three persons of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound that the melt resistivity value is lowered.

[0051]

The content of the alkali metal compound in a film, It is preferred to use more than 0 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline metal atom  $M^1$ , it is more preferred to be referred to as not less than 5 ppm, it is still more preferred to be referred to as not less than 6 ppm, and especially the thing set to not less than 7 ppm is preferred. Even if it increases content of an alkali metal compound too much, the reduction effect of a melt resistivity value is saturated and the generated amount of a foreign matter increases further. Therefore, as for the content of an alkali metal compound, it is preferred to be referred to as 100 ppm or less on the basis of alkaline metal atom  $M^1$ , it is more preferred to be referred to as 90 ppm or less, and it is still more preferred to be referred to as 80 ppm or less.



[0052]

As the above-mentioned alkaline earth metal compound, hydroxide of alkaline-earth metals, An alkoxide, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with the compound which has a phenolic hydroxyl group, etc. are mentioned. As alkaline-earth metals, magnesium, calcium, strontium, barium (preferably magnesium), etc. are mentioned. Magnesium acetate is contained especially in a desirable alkaline earth metal compound magnesium hydroxide, magnesium methoxide, magnesium acetate, calcium acetate, strontium acetate, barium acetate, etc. The above-mentioned alkaline earth metal compound is independent, or it can be used, combining it two or more sorts.

[0053]

As the above-mentioned Lynn content compound phosphoric acid (phosphoric acid, phosphorous acid, hypophosphorous acid, etc.). And the ester (alkyl ester, aryl ester, etc.) and alkyl phosphonic acid, aryl phosphonic acid, and those ester (alkyl ester, aryl ester, etc.) are mentioned. As desirable phosphorus compounds, it is aliphatic series ester (alkyl ester of phosphoric acid, etc.; for example) of phosphoric acid and phosphoric acid. Phosphoric acid mono-  $C_{1-6}$  alkyl ester, such as phosphoric acid monomethyl ester, phosphoric acid monoethyl ester, and phosphoric acid monobutyl ester, \*\*\*\*\*  $C_{1-6}$  alkyl ester, such as phosphodimethyl ester, phosphodi-ethyl ester, and dibutyl phosphate ester, Phosphoric acid Tori  $C_{1-6}$  alkyl ester, such as trimethyl phosphate ester, phosphoric acid triethyl ester, and tributyl phosphate ester etc., Aromatic ester (mono- \*\* JI or Tori  $C_{6-9}$  aryl ester of phosphoric acid, such as triphenyl phosphate and tricresyl phosphate, etc.) of phosphoric acid, aliphatic series ester of phosphorous acid (alkyl ester of phosphorous acid, etc.; for example) Mono- \*\* JI of phosphorous acid, such as phosphorous acid trimethyl \*\* phosphorous acid tributyl, or alkyl phosphonic acid ( $C_{1-6}$  alkyl phosphonic acid, such as methylphosphonic acid and ethylphosphonic acid) and alkyl phosphonic acid alkyl ester (dimethyl methylphosphonate.), such as Tori  $C_{1-6}$  alkyl ester Mono- \*\*\*\* of  $C_{1-6}$  alkyl phosphonic acid, such as ethyl dimethyl phosphonate, JI  $C_{1-6}$  alkyl ester etc., aryl phosphonic acid alkyl ester (dimethyl phenylphosphonate.) Mono- \*\*\*\* of  $C_{6-9}$  aryl phosphonic acid, such as diethyl phenylphosphonate, JI  $C_{1-6}$  alkyl ester etc., Aryl phosphonic acid aryl ester (mono- \*\*\*\* of  $C_{6-9}$  aryl phosphonic acid, such as diphenyl phenylphosphonate, is JI  $C_{6-9}$  aryl ester etc.) etc. can be illustrated. Phosphoric acid and phosphoric acid trialkyl (trimethyl phosphate etc.) are especially contained in the desirable Lynn content compound. These Lynn content compound is independent, or

it can be used, combining it two or more sorts.

[0054]

As the above-mentioned alkali metal compound, hydroxide of an alkaline metal, carbonate, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with the compound which has a phenolic hydroxyl group, etc. are mentioned. Lithium, sodium, potassium (preferably sodium), etc. are mentioned as an alkaline metal. Sodium acetate is contained especially in a desirable alkaline earth metal compound lithium hydroxide, sodium hydroxide, a potassium hydrate, lithium carbonate, sodium carbonate, potassium carbonate, lithium acetate, sodium acetate, potassium acetate, etc.

[0055]

The heat contraction nature polyester system film of this invention has an ester unit formed from a polyvalent carboxylic acid component and a polyhydric alcohol component as a main component unit.

[0056]

As polyvalent carboxylic acid for forming a polyvalent carboxylic acid component in an ester unit, Aromatic dicarboxylic acid, such as terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and aliphthalic acid; Adipic acid, Aliphatic dicarboxylic acid, such as azelaic acid, sebacic acid, and decane dicarboxylic acid; these ester formation derivatives, such as alicyclic dicarboxylic acid, are mentioned.

[0057]

When using above-mentioned aliphatic dicarboxylic acid, it is preferred that polyvalent carboxylic acid component 100 mol % of a film and an aliphatic dicarboxylic acid component are less than [ 3 mol % ]. Although mentioned later for details, in order to demonstrate tear-proof nature, intensity, heat resistance, etc. in the heat contraction nature polyester system film of this invention, it is desirable to use an ethylene terephthalate unit as a main component unit. Therefore, although it is recommended that a terephthalic acid component serves as a subject, the polyvalent carboxylic acid component in a film, When the amount of aliphatic dicarboxylic acid components is more than 3 mol %, in the heat contraction nature label obtained from this film, only the rigidity (waist of a film) which can be equal to high-speed wearing in a container may not be obtained.

[0058]

As for the polyvalent carboxylic acid (for example, trimellitic acid, pyromellitic acid, these anhydrides, etc.) more than trivalent, not using is preferred. In the heat

contraction nature polyester system film which has these polyvalent carboxylic acid components, sufficient heat shrinkage rate may become is hard to be acquired.

[0059]

As a polyhydric alcohol class for forming a polyhydric alcohol component in an ester unit, in order to form an ethylene terephthalate unit, ethylene glycol is used. In addition, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, Aliphatic series diol, such as 2-methyl-1,5-pentanediol and 2,2-diethyl-1,3-propanediol, Alicyclic diol, such as 1,4-cyclohexane dimethanol, dimer diol, a bisphenol compound, or the alkylene oxide adduct of the derivative can be used together.

[0060]

the film of this invention — diol (for example, propylene glycol.) of the carbon numbers 3-6 It is preferred to use one or more sorts and the polyester which adjusted glass transition temperature (T<sub>g</sub>) to 60-75 \*\* using 1,4-cyclohexane dimethanol among 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, etc.

[0061]

It is desirable to use especially the polyester which used neopentyl glycol together in respect of reservation of each of above-mentioned heat shrinkage rates, the improvement in contraction result appearance, and container reinforcing effect reservation. polyhydric alcohol component % of 100 mol of a film — inside and a neopentyl glycol component amount — more than 15 mol % — it is more than 18 mol % preferably, and it is recommended less than 27 mol % and that it is less than 25 mol % preferably. moreover — the case where diol of carbon numbers 3-6 other than neopentyl glycol is used — polyhydric alcohol component % of 100 mol of a film — inside and these diol components — more than 3 mol % — it is more than 5 mol % preferably, and it is desirable less than 15 mol % and that it is less than 13 mol % preferably. In addition, in the case where 1 and 4-cyclohexane dimethanol is used. polyhydric alcohol component % of 100 mol of a film — inside and 1 and 4-cyclohexane dimethanol component amount — more than 15 mol % — it is more than 18 mol % preferably, and less than 27 mol % and using less than 25 mol % preferably are recommended.

[0062]

As for diol (for example, octanediol etc.) of eight or more carbon numbers except the suitable polyhydric alcohol class of the above-mentioned illustration, and polyhydric alcohol more than trivalent, not using is preferred. In the heat contraction nature polyester system film which has these diol components and polyhydric alcohol

components, sufficient heat shrinkage rate may become is hard to be acquired.

[0063]

Although it is not a polyhydric alcohol class, a part of lactone represented by epsilon-caprolactone may be used. Lactone serves as a unit which carries out ring breakage and has an ester bond to both ends.

[0064]

If the tear-proof nature of a film, intensity, heat resistance, etc. are taken into consideration, it is preferred to choose so that component unit 100 mol % Naka of a heat contraction nature polyester system film and an ethylene terephthalate unit may become more than 50 mol %. Therefore, it is preferred to make more than 50 mol %, polyhydric alcohol component 100 mol % Naka, and an ethylene glycol component more than 50 mol % for polyvalent carboxylic acid component 100 mol % Naka and a terephthalic acid component (ingredient which consists of terephthalic acid or its ester). More than 55 mol % of an ethylene terephthalate unit is more preferred, and more than its 60 mol % is still more preferred.

[0065]

Although the polyester which constitutes a heat contraction nature polyester system film can be manufactured by carrying out melt polymerization with a conventional method, . Carry out the polycondensation of the oligomer by which the direct reaction of polyvalent carboxylic acid and the polyhydric alcohol class might be carried out. After carrying out the ester exchange reaction of what is called a direct polymerization method, and the methyl ester object and polyhydric alcohol of polyvalent carboxylic acid, what is called an ester interchange method etc. that carry out a polycondensation are mentioned, and arbitrary manufacturing methods can be applied. It may be polyester obtained by other polymerization methods. The degree of polymerization of polyester is made into intrinsic viscosity, and is preferred. [ of the thing of 0.3 - 1.3 dl/g ]

[0066]

As a polymerization catalyst, can use conventional various catalysts, and For example, a titanium system catalyst, An antimony system catalyst, a germanium system catalyst, a tin series catalyst, a cobalt system catalyst, Titanium system catalysts (titanium tetrabutoxide etc.), antimony system catalysts (antimonous oxide etc.), a germanium system catalyst, cobalt (diacid-ized germanium etc.) system catalysts (cobaltous acetate etc.), etc. are mentioned preferably a manganese system catalyst etc.

[0067]

The addition stage in particular of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound is not limited, Before an esterification reaction and during esterification, although it may be which stage from the end of esterification before a polymerization process start, under polymerization, and after a polymerization, it is from the end of esterification before a polymerization process start preferably to the desirable arbitrary stages after an esterification process, and a pan. If an alkaline earth metal compound and the Lynn content compound (and accepting necessity alkali metal compound) are added after an esterification process, the generated amount of a foreign matter can be reduced compared with the case where it adds before it.

[0068]

If needed, particles, such as silica, a titanium dioxide, kaolin, and calcium carbonate, may be added to a film material, and an antioxidant, an ultraviolet ray absorbent, a spray for preventing static electricity, colorant, an antimicrobial agent, etc. can also be added further.

[0069]

Although polyester film can be obtained by the publicly known method of mentioning later, In a heat contraction nature polyester system film, there are a method which performs copolymerization and carries out single use of this copolymerized polyester as a means to make two or more ingredients contain in a film, and a method which blends different gay polyester or copolymerized polyester of a kind.

[0070]

What is necessary is just to use the copolymerized polyester obtained from the polyhydric alcohol class of a predetermined presentation, and the polyvalent carboxylic acid of a predetermined presentation in the method which carries out single use of the copolymerized polyester. In the method which blends polyester of a different presentation on the other hand, since the characteristic of a film can be easily changed only by changing a blend ratio and it can respond also to the industrial production of the film of a various kind, it is preferably employable.

[0071]

It is preferred to specifically blend and use two or more sorts of polyester in which  $T_g(s)$  differ in the blending method. The polyester to blend may be three or more sorts.

[0072]

By blending and using two or more sorts of polyester, polyester does not dissolve but we are anxious about the trouble of a film milking, for example. However, the ester exchange reaction arose by being heated in the film extrusion process mentioned later,

and as a result of the polyester contained in a film turning into copolymerized polyester, it has usually become clear that troubles, such as the above-mentioned white blush mark, are avoided. Tg measured by the publicly known method about the film obtained from two or more sorts of polyester blends in which Tg(s) differ, for example can check copolymer-ization by such an ester exchange reaction from becoming a single value.

[0073]

It dries using dryers, such as a hopper dryer and a paddle dryer, or a vacuum dryer as a manufacturing method of a concrete film, and a raw material polyester chip is extruded to film state at the temperature of 200-300 °C using an extrusion machine. Or an undried polyester raw material chip is similarly extruded to film state, removing moisture within a vent type extruder. On the occasion of extrusion, a T-die method, a tubular method, etc. may adopt any existing method. After extrusion is quenched and obtains an unstretched film. The film on which tension required for the film advance in a manufacturing process acted is also contained in an unstretched film here.

[0074]

Although the film which consists of a single layer may be sufficient as the film of this invention, it may be a laminated film which laminated two or more layers (for example, two-layer, three layers, four etc. layers, etc.). When considering it as a laminated film, polyester of the same presentation as each class may be adopted, but it is also preferred to use polyester of a different presentation for every layer. In the case where it is considered as three layers, a central layer is also recommended having composition using polyester of other presentations using polyester of the presentation same to both outer layers. Although the laminating method in particular in the case of considering it as such a laminated film is not limited, the method of obtaining the above-mentioned unstretched film is employable by the publicly known co-extruding method etc., for example.

[0075]

As mentioned above, an electrode is allocated between the above-mentioned extrusion machine and a casting roll, voltage is impressed between an electrode and a casting roll, and it is recommended also in that sticking a film on a roll electrostatically attains equalization of the thickness distribution of a film.

[0076]

Stretching treatment is performed to the above-mentioned unstretched film. After cooling by the above-mentioned casting roll etc., stretching treatment may be performed continuously, is once rolled round to rolled form after cooling, and is good in

backward [ the ]. On productive efficiency, since it is practical that a maximum shrinkage direction is the direction of film width (width), it shows the example of the method of extending in the case of making a maximum shrinkage direction into a transverse direction hereafter. Also when making a maximum shrinkage direction into the direction of film length (straight side), changing 90 degrees etc. can extend the extension direction in the following method according to normal operation.

[0077]

If it notes making the thickness distribution of a heat contraction nature polyester system film equalize, and below the above-mentioned upper limit carrying out, When extending in a transverse direction using a tenter etc., it is preferred to perform a preheating process in advance of a stretching process, and in this preheating process. It is preferred to heat until it reaches a certain temperature within the limits whose film surface temperature is  $T_g+0$  \*\* $-T_g+60$  \*\* at a low wind speed so that thermal conductance may become in below  $0.00544 \text{ J/cm}^2 \cdot \text{sec}$ , and \*\* ( $0.0013\text{-calorie/cm}^2 \cdot \text{sec}$ , and\*\*).

[0078]

Lateral extension is performed with the prescribed temperature of  $T_g-5$  \*\* $-T_g+15$  \*\* within the limits. What is necessary is to divide extension into two or more steps, and just to perform it in the film of this invention, in order to carry out the above (A), the heat shrinkage rate of (B), and the heat shrinkage rate difference  $\Delta$  in a mentioned range and to carry out the above-mentioned maximum-heat-shrinkage-stress value in a mentioned range further. Hereafter, it explains taking the case of the case where it extends in two steps.

[0079]

First, the 1st step of extensions are performed. Draw magnification is preferably made into 5.5 or less times 4.8 or more times 6.0 or less times 4.4 or more times to an unstretched film. The 1st step of extension temperature is made into the above-mentioned temperature (prescribed temperature of  $T_g-5$  \*\* $-T_g+15$  \*\* within the limits).

[0080]

Next, it is preferred to perform heat setting, where a film is strained in the extension direction. Making the stress rate in that case into 5% or less not less than 2% preferably 6% or less 1% or more to the film after the 1st step of extensions is recommended. Heat setting temperature carries out [ about  $1-5$  \*\* / temperature / the 1st step of / extension ] whether it is made the same as the 1st step of extension temperature in the above-mentioned temperature requirement, and, as for heat

setting time, it is desirable for 3 or less seconds to take 1 second or more preferably 5 or less seconds 0.5 second or more.

[0081]

Next, the 2nd step of extensions are performed. Draw magnification is made into 1.5 or less (preferably 1.3 or less times) times 1.1 or more times to the film after heat setting (after [ when not carrying out heat setting ] the 1st step of extensions). As for the 2nd step of extension temperature, it is preferred to carry out [ about 1-5 \*\* / temperature / heat setting ] whether it is made the same as heat setting temperature in the above-mentioned temperature requirement.

[0082]

Then, applying stress slightly [ it is desirable and ] on a film, it cools and a heat contraction nature polyester system film is obtained. As for the stress rate at the time of cooling, it is preferred to consider it as 0.1 to 3% to the film after the 2nd step of extensions.

[0083]

When making the process of extension into a three-stage, it is desirable to put in the above-mentioned heat setting process between the 2nd step of extensions and extension of a three-stage eye. What is necessary is just to determine the conditions of a heat setting process according to the above-mentioned heat setting conditions. What is necessary is just to also determine the extension conditions of a three-stage eye according to the 2nd step of above-mentioned extension conditions.

[0084]

Since the design of the extension equipment in industrial production becomes difficult from viewpoints of heat shrinkage rate control of a film, etc. when there are not much too many step numbers although more ones of the step number of extension are preferred, it is desirable to consider it as four or less steps preferably six or less steps.

[0085]

In this lateral orientation process, it is preferred to use the equipment which can make change of film surface temperature small. Namely, although there are the preheating process before extension, a stretching process, a heat treatment process after extension, relaxing treatment, a re-stretching treatment process, etc. in a stretching process, it is preferred that the range of fluctuation of the skin temperature of the film especially measured in an optional point in a preheating process, a stretching process, and the heat treatment process after extension is the mean temperature of less than \*\*1 \*\*, and it is still more desirable if it is less than \*\*0.5 \*\* in mean temperature. When the range of fluctuation of the skin temperature of a film is small, it is to cover a



film overall length, to be extended and heat-treated at the same temperature, and for the physical properties of a heat contraction action or others to equalize.

[0086]

As the method of extension, 1.1 times - 2.0 times as many extensions may be preferably given to not only the width 1 axis extension by a tenter but a lengthwise direction 1.0 time - 4.0 times. Thus, when performing biaxial extension, any of biaxial extension and simultaneous biaxial extension may be sufficient one by one, and re-extension may be performed if needed. In biaxial extension, which methods, such as every direction, length-and-breadth, in every direction length, and length-and-breadth width, may be used as an order of extension one by one. Also in the case where these vertical stretching processes or a biaxial stretching process is adopted, it is preferred like lateral orientation to make change of film surface temperature as small as possible in a preheating process, a stretching process, etc.

[0087]

As equipment which can make small change of the above-mentioned film surface temperature, For example, in order to control the wind speed of the hot wind which heats a film, an inverter is attached, and the equipment which can control change of a wind speed, the equipment which uses low-pressure steam of 500 or less (below 5 kgf/cm<sup>2</sup>) kPa for a heat source, and can control the temperature change of a hot wind, etc. are mentioned.

[0088]

As for the coefficient of heat transfer of a stretching process, if the point which controls internal generation of heat of the film accompanying extension, and makes crosswise film temperature spots small is noted, it is preferred to use more than 0.00377 J/cm<sup>2</sup>, sec, and \*\* (0.0009-calorie/cm<sup>2</sup>, sec, and\*\*). 0.00544 - 0.00837 J/cm<sup>2</sup>, sec, and \*\* (0.0013-0.0020-calorie/cm<sup>2</sup>, sec, and\*\*) are more preferred.

[0089]

And in the polyester system film of this invention. In order to secure ultraviolet-rays cut nature and a natural light transmittance state predetermined [ above-mentioned ], a film is made to contain ultraviolet-rays cut agents (a low molecule system ultraviolet-rays cut agent, the Polymer Division system ultraviolet-rays cut agent, an inorganic system ultraviolet-rays cut agent, etc.), and a kind, a content gestalt, etc. of an ultraviolet-rays cut agent are chosen appropriately. Hereafter, it divides into the kind of ultraviolet-rays cut agent, and explains to details more.

[0090]

(1) When a low molecule system ultraviolet-rays cut agent is used

A low molecule system ultraviolet-rays cut agent is an ultraviolet-rays cut agent of the organic system which can absorb ultraviolet rays, and since the refractive index to visible light approximates with the polyester system film, there is no possibility of reducing a natural light transmittance state. However, sufficient ultraviolet-rays cut nature may not be obtained for the Reasons of heat resistance being low and/or a low molecule system ultraviolet-rays cut agent having sublimability under high temperature service. For example, a low molecule system ultraviolet-rays cut agent is scoured in melting-like polyester, Although it is made to contain in a film in many cases by the method (film chemically-modified degree) of film-izing by extrusion molding etc., in order that a low molecule system ultraviolet-rays cut agent may decompose or sublimate at the time of the above-mentioned kneading lump and extrusion molding, The ultraviolet-rays cut nature of a film may fall, or manufacturing facilities (casting roll used at the time of film production) may be polluted.

[0091]

Then, in this invention, in using a low molecule system ultraviolet-rays cut agent, The thing of the layer (an internal layer is called hereafter) which decides to form the laminated film of two or more layers (for example, three or more-layer layers, three layers, four layers, five etc. layers, etc.), and does not form a surface layer by the co-extruding method etc. which were mentioned above made to in part or all (preferably all) contain a low molecule system ultraviolet-rays cut agent is desirable. If an internal layer is made to contain a low molecule system ultraviolet-rays cut agent, sublimation of an ultraviolet-rays cut agent can be prevented at least, and the yield of the ultraviolet-rays cut agent of a film chemically-modified degree can be raised. Therefore, the ultraviolet-rays cut nature of a film can be improved, and contamination of a manufacturing facility can be prevented. A surface layer may be made to contain an ultraviolet-rays cut agent, and it is not necessary to make it contain.

[0092]

(2) When the Polymer Division system ultraviolet-rays cut agent is used

It is an ultraviolet-rays cut agent of the organic system which can absorb ultraviolet rays, and since the refractive index to visible light also approximates the Polymer Division system ultraviolet-rays cut agent (polymer system ultraviolet-rays cut agent) with the polyester system film, it does not have a possibility of reducing a natural light transmittance state. [ as well as the above-mentioned low molecule system ultraviolet-rays cut agent ] Unlike the above-mentioned low molecule system ultraviolet-rays cut agent, the Polymer Division system ultraviolet-rays cut agent is

excellent in respect of heat resistance. Therefore, the pyrolysis of a film chemically-modified degree can be prevented and the yield of an ultraviolet-rays cut agent can be raised. Therefore, when using the Polymer Division system ultraviolet-rays cut agent, the polyester system film of a monolayer may be made to contain an ultraviolet-rays cut agent.

[0093]

When using the Polymer Division system ultraviolet-rays cut agent, a part or all (preferably all) of an internal layer may be made to contain an ultraviolet-rays cut agent like the case where the above-mentioned low molecule system ultraviolet-rays cut agent is used. If an internal layer is made to contain an ultraviolet-rays cut agent, even if it is a case where the Polymer Division system ultraviolet-rays cut agent has sublimability, the yield of an ultraviolet-rays cut agent can be raised and the ultraviolet-rays cut nature of a film can be improved. Contamination of a manufacturing facility can be prevented.

[0094]

(3) When an inorganic system ultraviolet-rays cut agent is used

The inorganic system ultraviolet-rays cut agent can omit ultraviolet rays by intercepting ultraviolet rays. Since this cut agent is excellent in heat resistance, it is excellent in the yield of a film chemically-modified degree, and can improve the ultraviolet-rays cut nature of a film easily. However, since the refractive index to visible light is different from the polyester system film unlike the above-mentioned organic system ultraviolet-rays cut agents (a low molecule system ultraviolet-rays cut agent, the Polymer Division system ultraviolet-rays cut agent, etc.), an inorganic system ultraviolet-rays cut agent has a possibility of reducing a natural light transmittance state.

[0095]

Then, in this invention, in using an inorganic system ultraviolet-rays cut agent, it uses the particle-like cut agent whose mean particle diameter is shorter than the wavelength of visible light. Ultraviolet rays can be omitted without reducing a natural light transmittance state, if an inorganic particle-like system ultraviolet-rays cut agent is used.

[0096]

the mean particle diameter of an inorganic system ultraviolet-rays cut agent — for example — 100 nm or less of 70 nm or less is 40 nm or less still more preferably preferably. The mean particle diameter of an inorganic system ultraviolet-rays cut agent is usually not less than 10 nm.

[0097]

When using an inorganic system ultraviolet-rays cut agent, a part or all (preferably all) of an internal layer may be made to contain an ultraviolet-rays cut agent like the case where the above-mentioned low molecule system ultraviolet-rays cut agent is used. If an internal layer is made to contain an ultraviolet-rays cut agent, even if it is a case where an inorganic system ultraviolet-rays cut agent has sublimability, the yield of an ultraviolet-rays cut agent can be raised and the ultraviolet-rays cut nature of a film can be improved.

[0098]

Although a film may be made to contain an ultraviolet-rays cut agent (an organic system ultraviolet-rays cut agent, an inorganic system ultraviolet-rays cut agent) by the method of \*\*\*\* scouring, and applied or impregnating with methods other than a lump, for example, a film, it is more preferred to make a film contain by scour lump. According to the scour lump, thickness of an ultraviolet ray cutting layer can be thickened and the ultraviolet-rays cut nature of a film can be improved.

[0099]

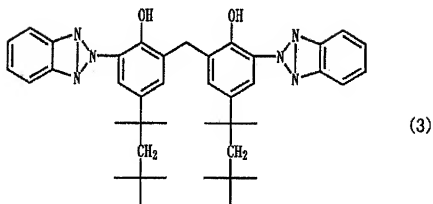
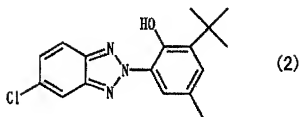
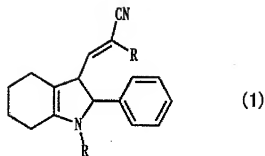
although the content of the ultraviolet-rays cut agent in a polyester system film can be suitably chosen according to the kind of ultraviolet-rays cut agent — a 0.1 - 50 mass % grade — desirable — a 0.3 - 40 mass % grade — it is a 0.5 - 30 mass % grade still more preferably. in addition — when using a low molecule system ultraviolet-rays cut agent, the maximum of said amount used may be smaller — for example, a maximum — a 10 mass % grade — it may be a 5 mass % grade preferably.

[0100]

As a low molecule system ultraviolet-rays cut agent, for example An indole series ultraviolet-rays cut agent [compound etc. which are expressed with following formulas (1), such as "BONASOPU 3901" by an Orient chemicals company etc.], A benzotriazol system ultraviolet-rays cut agent [compound etc. which are expressed with following formulas (3), such as "LA-31" by a compound; Asahi electrification company etc. expressed with following formulas (2), such as the "tinuvin 326" by Ciba Specialty Chemicals etc.], A benzophenone series ultraviolet-rays cut agent, a cyanoacrylate system ultraviolet-rays cut agent, a phenyl salicylate system ultraviolet-rays cut agent, etc. are mentioned.

[0101]

[Formula 1]



[0102]

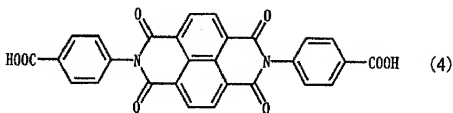
(R shows an alkyl group among a formula)

As a Polymer Division system ultraviolet-rays cut agent, the Polymer Division system ultraviolet-rays cut agent of various common use can be used. The polymer obtained from ultraviolet absorbability monomers (NAFUTARU imide system compound etc.) is contained in the desirable Polymer Division system ultraviolet-rays cut agent. For example, copolymerized polyester containing the NAFUTARU imide system compound expressed with naphthalene dicarboxylic acid and a following formula (4), such as

"nova PEKKUSU (by Mitsubishi Chemical, Inc. etc.) U110", can be used as an acid component.

[0103]

[Formula 2]



[0104]

As an inorganic system ultraviolet-rays cut agent, titanium system ultraviolet-rays cut agents (titanium oxide etc.) etc. are mentioned.

[0105]

Although the thickness in particular of the heat contraction nature polyester system film of this invention is not limited, as a heat contraction nature polyester system film for labels, 10-100 micrometers is preferred and 20-60 micrometers is still more preferred, for example.

[0106]

Even if it uses a heat contraction nature label obtained using a heat contraction nature polyester system film of this invention for full labels (label that high contraction is required selectively), such as a PET bottle, it can present good contraction result appearance. It can become high contraction by short-time processing. It also has an effect of reinforcing containers, such as a PET bottle by which covering contraction was carried out.

[0107]

In order to use the above-mentioned heat contraction nature polyester system film as a heat contraction nature label, For example, it takes out, after carrying out predetermined time storage of the heat contraction nature film before contraction into environment which controlled temperature and humidity, Using publicly known tube shape molding equipment, a film is rounded off promptly, and an end is piled up, and it pastes [ a solvent for adhesion is applied inside with prescribed width for a while from the edge of one side of a film piece end, and ] up, and is processed into a tube.

This tube can be cut out to predetermined length and it can be considered as a heat contraction nature label of this invention.

[0108]

As for adhesion of a film, although it is also possible to adopt a melt adhesion method to which melting of a part of film is carried out, it is preferred to carry out from a viewpoint of controlling change of the heat contraction characteristic of a label, etc., using a solvent. As a solvent which can be used, for example Benzene, toluene, xylene, Aromatic hydrocarbon, such as trimethyl benzene; although organic solvents, such as oxo orchid species [, such as franc; 1,3-dioxolanes, such as phenols; tetrahydrofurans, such as halogenated hydrocarbon; phenol such as a methylene chloride and chloroform, ], are mentioned, Especially, 1,3-dioxolane is desirable at a point that safety is high.

[0109]

After equipping containers, such as a PET bottle, with the above-mentioned heat contraction nature label, heat contraction of it can be carried out and it can be made to cover with publicly known heat contraction means (a hot wind tunnel, a steam tunnel, etc.) which were mentioned above.

[0110]

Even if weight is about 30% lower than the conventional PET bottle, a PET bottle which carried out covering contraction of the heat contraction nature label of this invention is reinforced, for example to such an extent that it can be dealt with like the conventional PET bottle, for example in the cases, such as transportation and sale. It is preferred that not less than 75% of drum section surface area of a PET bottle is covered with a label in this case.

[0111]

For example, in a label produced from a heat contraction nature film of this invention by performing it as follows, preferably, a diameter rate of change of a bottle measured by an after-mentioned method is 7% or less more preferably, and can demonstrate an outstanding container reinforcing effect 10% or less.

[0112]

After applying 1,3-dioxolane inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm<sup>2</sup>) and piling up this end, it judges in 14 cm in length, and size 6.7 cm in diameter, and a cylindrical label is obtained. It seals, after filling up a 500mL round shape PET bottle [21 cm in height, and center-section (drum section) 6.5 cm in diameter] with a mass of 20.5 g with water of 500mL, and this is equipped with the above-mentioned cylindrical label, a steam tunnel with a zone

temperature of 85 °C is passed in 2.5 seconds, and this label is shrunk. Thus, a path ( $W_1$ ) of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for a side center section of the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and a diameter rate of change of a bottle (%) is searched for according to a following formula. Diameter rate of change of a bottle (%) =  $100 \times (W_1 - W_2) / W_2$

Here,  $W_2$  is a path of a bottle center section before imposing load.

[0113]

Since it is easy to transform this container and may become causes, such as plugging, in a label that the above-mentioned diameter rate of change of a bottle exceeds 10% when a covering container falls, for example within a vending machine, it is not desirable.

[Example]

[0114]

Hereafter, although this invention is further explained in full detail according to working example, following working example does not restrict this invention, and when carrying out change implementation in the range which does not deviate from the meaning of this invention, it is included in this invention. "ppm" used by this example is a mass basis. The measuring method of the physical properties of the film obtained by working example and a comparative example is as follows.

[0115]

(1) Heat shrinkage rate

Cut out a film in square of 10 cm x 10 cm, and in the warm water of the temperature of following (A), (B), and (C). After being immersed for 5 seconds and carrying out heat contraction by no load condition, it is made to be immersed in 25 °C underwater [ ±0.5 °C ] for 10 seconds, and it pulls out from this underwater one, the length of a sample and lateral length are measured, and it asks according to a following formula. Heat shrinkage rate (%) =  $100 \times (\text{length after the length-contraction before contraction}) / (\text{length before contraction})$

Here, they are (A): 75 °C ±0.5 °C, (B): 85 °C ±0.5 °C, and (C): 95 °C ±0.5 °C. Let a direction with the largest contraction be a maximum shrinkage direction.

[0116]

(2) Heat shrinkage rate difference

The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum



shrinkage direction. The film after decision is fixed with a described [ above ] type. Immobilization is performed by slacking a film so that the both ends which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 °C warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 °C underwater [ 0.5 °C ], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained. Then, in the state of an atony, this film is placed in the air and under the environment of 25 °C or less, and the following process is presented as much as possible with it for a short time.

[0117]

Judge this film in square of 10 cm x 10 cm, and in 95 °C warm water, After being immersed for 5 seconds and carrying out heat contraction by no load condition, it is made to be immersed in 25 °C underwater [ 0.5 °C ] for 10 seconds, and it pulls out from this underwater one, the length of a sample and lateral length are measured, and it asks for heat shrinkage rate  $X_{10}$  of a maximum shrinkage direction according to the above-mentioned heat shrinkage rate formula. The heat shrinkage rate of the maximum shrinkage direction called for on condition of (C) of the above (1) is made into  $X_0$ . From these values, the heat shrinkage rate difference  $\Delta$  (%) is computed according to an upper type (1).

[0118]

### (3) Ultraviolet ray transmission

A film is judged in shape of 38 mm x 13 mm, this decision film is set to a double beam spectrophotometer ("U-2001" By Hitachi), and the ultraviolet ray transmission of a prescribed wavelength (380 nm, 400 nm) is measured.

[0119]

### (4) Hays

According to JIS K 7105, Hays of a film is measured using an integrating sphere type light transmission measuring device ("1001DP" by Japan electric-spectaculars industrial incorporated company).

[0120]

### (5) Maximum-heat-shrinkage-stress value

It measures using a tension tester with a heating furnace (the "tensilon" by Oriental energy machine incorporated company). From the film before heat contraction, at 200

mm, start a 20-mm-wide sample, and the length of a maximum shrinkage direction stops air blasting of the tension tester beforehand heated at 90 \*\*, makes a sample the distance between zippers of 100 mm, and it The length between zippers of a specimen, After the distance between zippers slacks a specimen and attaches it so that it may be set to 1:0.9, The door of a heating furnace is shut promptly, the contraction stress detected in a 5 m [ in (temperature of 90 \*\* and blow-off speed ]/second hot wind when supply) is started from the three way of the back, the left, and the right is measured, and the maximum-heat-shrinkage-stress value (MPa) after 10% contraction is calculated from a measurement chart.

[0121]

#### (6) Thickness distribution

Ten specimens which make the maximum shrinkage direction of a film the length direction are created at 50 cm in length, and 5 cm in width, About each specimen, contact process thickness meters, such as for example, "KG60/A" (by ANRITSU CORP. etc.), are used, The thickness of the length direction is measured continuously and it outputs to a chart, and from this output, after asking for maximum thickness, the minimum thickness, and average thickness and computing thickness distribution using an upper type (2) from these, the average value of the thickness distribution of ten specimens is calculated, and it is considered as the thickness distribution of a film.

[0122]

#### (7) Melt resistivity value

The electrode plate of a couple is inserted into the sample (film) fused at the temperature of 275 \*\*, and the voltage of 120V is impressed. The current in that case is measured and melt resistivity value  $S_i$  (ohm-cm) is computed based on a lower type.

$$S_i = (A/I) \times (V/i_o)$$

here -- area [ of A:electrode ] (cm<sup>2</sup>), and l:inter electrode distance (cm) V:voltage (V), and  $i_o$  -- it is current (A).

[0123]

#### (8) Contraction result nature

3 color prints are carried out to a film in the green by TOYO INK MFG. CO., LTD., and golden and white ink, It takes out, after keeping it for 250 hours in the environment controlled to the temperature of 30\*\*1 \*\*, and 85\*\*2% of relative humidity, Using tube shape molding equipment, 1,3-dioxolane is applied inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm<sup>2</sup>), and a film is rounded off promptly, and an end is piled up, and it pastes up, is considered as a tube, and rolls round in the state where it crushed level. This tube is cut out and it is

considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. 500mL round shape PET bottle [21 cm in height made to fill up this label with water. Center-section (drum section) 6.5-cm] is equipped, the label whole quantity is passed for under the steam tunnel by FUJII ASTEC Co., Ltd. (SH-1500-L) on conditions with a zone temperature of 85 °C for tunnel pass time 2.5 seconds, and a label is shrunk (n= 20). [ in diameter ] The grade of a contraction result is judged visually and contraction result nature is evaluated in two steps. Generating nothing, wrinkles, a jump, or the shortage of contraction considers as generating all in which the standard of O:wrinkles, a jump, and contraction is insufficient.

[0124]

#### (9) Container reinforcing effect

Using tube shape molding equipment, 1,3-dioxolane is applied inside by 3mm-width for a while from the edge of one side of one end of a film (coverage: 3.0\*0.3g/mm<sup>2</sup>), and a film is rounded off promptly, and an end is piled up, and it pastes up, is considered as a tube, and rolls round in the state where it crushed level. This tube is cut out and it is considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. Mass : It seals, after filling up a 20.5-g 500mL round shape PET bottle [21 cm in height, and center-section (drum section) 6.5 cm in diameter] with the water of 500mL, This is equipped with the above-mentioned cylindrical label, the label whole quantity is passed for under the steam tunnel by FUJII ASTEC Co., Ltd. (SH-1500-L) on conditions with a zone temperature of 85 °C for tunnel pass time 2.5 seconds after that, and a label is shrunk.

[0125]

Thus, the path ( $W_1$ ) of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for the side center section of the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and the diameter rate of change of a bottle (%) is searched for according to a following formula.

$$\text{Diameter rate of change of a bottle (\%)} = 100 \times (W_1 - W_2) / W_2$$

Here,  $W_2$  is a path of the bottle center section before imposing load.

[0126]

#### The synthetic example 1

Between esterification reactions, as polyvalent carboxylic acid, dimethyl terephthalate 100 mol %, Ethylene glycol 100 mol % is taught by 2.2 times (mole ratio) to polyvalent carboxylic acid as a polyhydric alcohol class, Temperature up was carried out to 230 °C, having taught simultaneously and agitating antimonous oxide to polyvalent

carboxylic acid, as a catalyst, so that it may be set to 81 ppm by Mg atom conversion 0.04-mol% to the polyester which has magnesium acetate 4 hydrate formed, and the ester exchange reaction was performed by ordinary pressure for 120 minutes. The end of the ester exchange reaction was considered as the place which methanol of the specified quantity distilled off. The polycondensation reaction was performed for about 40 minutes, and the polyester A was obtained after the end of an ester exchange reaction until a temperature raising and melt viscosity became 7000 poise to 280 \*\*, decompressing [ added so that it might be set to 58 ppm to the polyester formed by P atom conversion, and ] trimethyl phosphate over 85 minutes.

[0127]

The synthetic examples 2-7

The polyester B-G shown in Table 1 was compounded like the synthetic example 1. In the synthetic examples 2 and 3, as a polymerization catalyst, antimonous oxide was used so that Sb atoms might be set to 160 ppm to polyester, and the polyester B and C was obtained. In the synthetic example 4, as a polymerization catalyst, titanium tetrabutoxide was used so that Ti atoms might be set to 90 ppm to polyester, and the polyester D was obtained. Furthermore, in the synthetic example 6, cobaltous acetate 4 hydrate is made for Mg atom to be set to 20 ppm to polyester as a polymerization catalyst, further, titanium tetrabutoxide was used so that Ti atoms might be set to 15 ppm to polyester, and the polyester F was obtained. In the synthetic example 7, it presupposed that it is the same as that of the synthetic example 1 about a polymerization catalyst, and the polyester G was obtained.

[0128]

Polyester A-G obtained in the above-mentioned synthetic examples 1-7 is shown in Table 1. The inside of Table 1, DMT:dimethyl terephthalate and DMN:dimethyl naphthalate, EG:ethylene glycol, NPG:neopentyl glycol, BD:1,4-butanediol, CHDM:1,4-cyclohexane dimethanol, PPG: It is a propanediol.

[0129]

[Table 1]

| ポリエステル | 仕込み組成         |     |     |               |     |      |     |
|--------|---------------|-----|-----|---------------|-----|------|-----|
|        | 多価カルボン酸類(モル%) |     |     | 多価アルコール類(モル%) |     |      |     |
|        | DMT           | DMN | EG  | NPG           | BD  | CHDM | PPG |
| A      | 100           | —   | 100 | —             | —   | —    | —   |
| B      | 100           | —   | 70  | 30            | —   | —    | —   |
| C      | 100           | —   | 60  | 40            | —   | —    | —   |
| D      | 100           | —   | —   | —             | 100 | —    | —   |
| E      | —             | 100 | 100 | —             | —   | —    | —   |
| F      | 100           | —   | 70  | —             | —   | 30   | —   |
| G      | 100           | —   | —   | —             | —   | —    | 100 |

[0130]

# Experiment 1

Lamination polyester system film No[ of three layers ].1 which consists of both outer layers and a central layer was obtained. Each chip of the polyester A, the polyester B, and the polyester D which carried out predrying to the central layer separately,

respectively is mixed at a rate shown in Table 2, Among a total of 100 mass % of mixed polyester and an ultraviolet-rays cut agent, it added and the ultraviolet-rays cut agent (the "tinuvin 326" by Ciba Specialty Chemicals) was used for this mixed polyester so that an ultraviolet-rays cut agent might become 1 mass %. The mixture of mixed polyester and the ultraviolet-rays cut agent of the same presentation as a central layer was used also for both outer layers. These mixed polyester chips were quenched with the casting roll a co-extrusion and after that at 280 °C using the single screw extruder which has a T die, and the thickness of both outer layers obtained the unstretched film of the three-tiered structure whose thickness of 65 micrometers and a central layer is 130 micrometers, respectively. After preheating this unstretched film for 3 seconds at 100 °C, it extended in the transverse direction (film width direction) by the tenter. First, extension is extended 4.75 times at 77 °C (the 1st step), subsequently was strained 3% to the film width at the time of the end of the 1st step for 5 seconds at 77 °C (heat setting), subsequently it is 75 °C, and was extended by 1.1 times the film width at the time of the end of heat setting (the 2nd step), and was performed. Subsequently, it cooled to the film width at the time of the 2nd step of ends of extension, applying 1% of stress, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.1 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0131]

#### Experiment 2

The mixture ratio of a polyester chip and the addition of the ultraviolet-rays cut agent were changed as shown in Table 2, and also the 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained like the experiment 1. About this unstretched film, it extended like the experiment 1 and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.2 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0132]

#### Experiment 3

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into

the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.3 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0133]

#### Experiment 4

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.4 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0134]

#### Experiment 5

As shown in Table 2, changed the mixture ratio of the polyester chip, changed the ultraviolet-rays cut agent into "BONASOPU 3901" by an Orient chemicals company further, as shown in Table 2, changed the addition of the ultraviolet-rays cut agent, and also it is made to be the same as that of the experiment 1, The 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.5 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0135]

#### Experiment 6

As shown in Table 2, changed the mixture ratio of the polyester chip, changed the ultraviolet-rays cut agent into "nova PEKKUSU U110" by Mitsubishi Chemical further, as shown in Table 2, changed the addition of the ultraviolet-rays cut agent, and also it is made to be the same as that of the experiment 1, The 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained. About this unstretched film, it changed into the conditions shown in Table 3, and also extended

like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.6 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0136]

#### Experiment 7

The mixture ratio of the polyester chip was changed as shown in Table 2, and also the 260 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained like the experiment 1. About this unstretched film, it extended like the experiment 1 and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.7 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0137]

#### Experiment 8

As shown in Table 2, changed the quantity of the ultraviolet-rays cut agent added in the mixed polyester used for a central layer, and an ultraviolet-rays cut agent was not added in both outer layers, and also the 26 micrometers (in the thickness of both outer layers, the thickness of 65 micrometers and a central layer is 130 micrometers, respectively)-thick unstretched film was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.8 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0138]

#### Experiment 9

As shown in Table 2, changed the mixture ratio of the polyester chip, and an ultraviolet-rays cut agent was not used in any of a central layer and both outer layers, and also the 260-micrometer (in thickness of both outer layers, thickness of 65-micrometer and central layer is 130 micrometers, respectively) unstretched film in thickness was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.9 was



obtained. The evaluation result of the obtained film is shown in Table 4.

[0139]

#### Experiment 10

In any of a central layer and both outer layers, an ultraviolet-rays cut agent was not used, and also the 200-micrometer (in thickness of both outer layers, thickness of 50-micrometer and central layer is 100 micrometers, respectively) unstretched film in thickness was obtained like the experiment 1. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.10 was obtained. The evaluation result of the obtained film is shown in Table 4.

[0140]

#### Experiment 11

Changed the ultraviolet-rays cut agent into  $\text{TiO}_2$  ("JR600A" by TAYCA CORP.) whose mean particle diameter is 0.25 micrometer, as shown in Table 2, changed the addition, and also. The 260-micrometer (in thickness of both outer layers, thickness of 50-micrometer and central layer is 100 micrometers, respectively) unstretched film in thickness was obtained like the experiment 1 like the experiment 1. To this unstretched film, it extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)-thick polyester system film No.11 was obtained to it. The evaluation result of the obtained film is shown in Table 4.

[0141]

[Table 2]

|            | ポリエステル重合組成(質量部) |    |    |    |    |    |    | 紫外線カット剤          |          |     |
|------------|-----------------|----|----|----|----|----|----|------------------|----------|-----|
|            | A               | B  | C  | D  | E  | F  | G  | 品名               | 添加量(質量%) |     |
|            |                 |    |    |    |    |    |    |                  | 中心層      | 両外層 |
| フィラムNo. 1  | 15              | 75 | —  | 10 | —  | —  | —  | チズピン326          | 1.0      | 1.0 |
| フィラムNo. 2  | 10              | 80 | —  | 10 | —  | —  | —  | チズピン326          | 0.5      | 0.5 |
| フィラムNo. 3  | 15              | 80 | —  | 5  | —  | —  | —  | チズピン327          | 1.0      | 1.0 |
| フィラムNo. 4  | 15              | —  | 75 | 10 | —  | —  | —  | チズピン328          | 1.0      | 1.0 |
| フィラムNo. 5  | —               | —  | —  | 15 | 85 | —  | —  | ボナソープ3901        | 0.5      | 0.5 |
| フィラムNo. 6  | 15              | —  | —  | —  | —  | 85 | —  | ノバベックスU110       | 30       | 30  |
| フィラムNo. 7  | 15              | —  | 75 | —  | —  | —  | 10 | チズピン328          | 1.0      | 1.0 |
| フィラムNo. 8  | 15              | 75 | —  | 10 | —  | —  | —  | チズピン328          | 1.5      | 0   |
| フィラムNo. 9  | 40              | —  | 50 | 10 | —  | —  | —  | —                | 0        | 0   |
| フィラムNo. 10 | 15              | 75 | —  | 10 | —  | —  | —  | —                | 0        | 0   |
| フィラムNo. 11 | 15              | 75 | —  | 10 | —  | —  | —  | TiO <sub>2</sub> | 5        | 5   |

[0142]

Polyester system film No.1 - No.11 are with a central layer and both outer layers as above-mentioned, and polyester mixture composition is common. Therefore, the "polyester mixture composition" column of Table 2 shows the polyester mixture composition of all the layers of a central layer and both outer layers. The ultraviolet-rays cut agent addition of Table 2 shows the quantity to a total of 100 mass % of mixed polyester and an ultraviolet-rays cut agent.

[0143]

[Table 3]

|            | 延伸条件      |            |            |            |           |           |            |
|------------|-----------|------------|------------|------------|-----------|-----------|------------|
|            | 延伸1段階目    |            | 熱固定        |            |           | 延伸2段階目    |            |
|            | 倍率<br>(倍) | 温度<br>(°C) | 緊張率<br>(%) | 温度<br>(°C) | 時間<br>(秒) | 倍率<br>(倍) | 温度<br>(°C) |
|            |           |            |            |            |           |           |            |
| フィルムNo. 1  | 4.75      | 77         | 3          | 77         | 5         | 1.1       | 75         |
| フィルムNo. 2  | 4.75      | 77         | 3          | 77         | 5         | 1.1       | 75         |
| フィルムNo. 3  | 4.75      | 80         | 3          | 80         | 5         | 1.1       | 78         |
| フィルムNo. 4  | 4.75      | 78         | 0          | —          | —         | 1.1       | 78         |
| フィルムNo. 5  | 4.75      | 95         | 3          | 75         | 5         | 1.1       | 75         |
| フィルムNo. 6  | 4.75      | 80         | 3          | 75         | 5         | 1.1       | 75         |
| フィルムNo. 7  | 4.75      | 77         | 3          | 77         | 5         | 1.1       | 75         |
| フィルムNo. 8  | 4.75      | 78         | 3          | 75         | 5         | 1.1       | 75         |
| フィルムNo. 9  | 4.75      | 84         | 0          | —          | —         | 1.1       | 77         |
| フィルムNo. 10 | 3.64      | 78         | 0          | —          | —         | 1.1       | 78         |
| フィルムNo. 11 | 4.75      | 77         | 3          | 77         | 5         | 1.1       | 75         |

[0144]

The draw magnification at the time of the 1st step of extensions the ratio to film width, and the stress rate in the case of heat setting among Table 3, A ratio [ as opposed to the film width after heat setting (after / when not carrying out heat setting / the 1st step extension) in the ratio to the film width after the 1st step of extensions and the draw magnification at the time of the 2nd step of extensions ], and the stress rate at

the time of cooling are ratios to the film width after the 2nd step of extensions. The stress rate "0%" of heat setting as used in film No.4, and 9 and 10 means having cooled the film, without the stress rate at the time of cooling "0%" applying stress for not having established the heat setting process after the 2nd step of extensions.

[0145]

[Table 4]

|        | 熱収縮率 (%) |            |             | 熱収縮率差<br>Δ (%) | 光線透過率 (%)   |      |  | ヘーズ<br>(%) | 最大<br>熱収縮<br>応力値<br>(MPa) | 収縮<br>仕上り性 | 厚み分布<br>(%) | 熔融<br>比抵抗値<br>( $\times 10^8$<br>$\Omega \cdot \text{cm}$ ) | ポトル径<br>変化率<br>(%) |
|--------|----------|------------|-------------|----------------|-------------|------|--|------------|---------------------------|------------|-------------|---|--------------------|
|        | (B)      |            | 波長<br>380nm |                | 波長<br>400nm |      |  |            |                           |            |             |   |                    |
|        | (A)      | 最大収縮<br>方向 |             |                |             | 直交方向 |  |            |                           |            |             |   |                    |
| No. 1  | 30       | 78         | -1          | 10             | 2           | 30   |  | 9          | 12                        | ○          | 0.8         | 0.32  | 6.0                |
| No. 2  | 43       | 78         | -3          | 11             | 13          | 51   |  | 9          | 12                        | ○          | 0.9         | 0.27  | 6.1                |
| No. 3  | 48       | 78         | -3          | 11             | 3           | 30   |  | 11         | 14                        | ○          | 0.7         | 0.31  | 5.9                |
| No. 4  | 30       | 76         | -2          | 15             | 2           | 31   |  | 9          | 8                         | ○          | 1.3         | 0.32  | 6.7                |
| No. 5  | 15       | 76         | 2           | 15             | 1.3         | 0.5  |  | 12         | 10                        | ○          | 1.0         | 0.65  | 6.5                |
| No. 6  | 13       | 76         | -1          | 16             | 0           | 52   |  | 11         | 14                        | ○          | 0.9         | 0.31  | 5.9                |
| No. 7  | 42       | 77         | 1           | 11             | 2           | 30   |  | 10         | 11                        | ○          | 1.1         | 0.41  | 6.3                |
| No. 8  | 30       | 78         | 0           | 10             | 0           | 20   |  | 9          | 12                        | ○          | 0.8         | 0.32  | 6.0                |
| No. 9  | 20       | 70         | 1           | 30             | 81          | 82   |  | 7          | 5                         | ×          | 2.0         | 0.55  | 10.2               |
| No. 10 | 17       | 74         | 8           | 26             | 80          | 82   |  | 6          | 6                         | ×          | 2.5         | 0.32  | 11.0               |
| No. 11 | 28       | 77         | -1          | 13             | 0           | 0    |  | 90         | 12                        | ○          | 0.9         | 0.32  | 6.0                |